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INVESTIGATION OF THE ISOTOPIC EXCHANGE OF BROMINE BETWEEN PROPYL BROMIDE AND SODIUM BROMIDE IN AN ALCOHOL SOLUTION

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/The methods described in this report are used in the enrichment of radioactive isotopes.

Tables and figures referred to are appended./

It was shown in our earlier studies of the kinetics of isotopic exchange (1-4) that the exchange of an iodine ion with the central iodine atom in KIO_3 requires a high activation energy of about 32,000 cal/mole. On the other hand, the exchange of iodine with the iodine atom in C_2H_5I proceeds in an alcohol solution with a low activation energy of the order of 19,000 cal/mole.

In the present work we have studied the kinetics of the exchange in an alcoholic solution of bromine ions with the bromine atoms in propyl bromide.

One of the first works on the isotopic exchange of bromine was published by S. Z. Roginskiy (5). The results of qualitative works on bromine exchange are stated in a review by S. Z. Roginskiy and N. Ye. Brezhneva (6). Several works on the kinetics of the isotopic exchange of bromine ions with alkylbromides of different structures have been published by Sugden. A summary of the results he obtained (7) shows that this exchange in different solvents proceeds with an activation energy lying within the limits of 18,000 to 23,000 cal/mole. The propyl bromide which we used was subjected to careful distillation, and its middle fraction, with a boiling point of 70.8° at 760 mm, was selected for the experiments.

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Radioactive bromine was produced by irradiating bromobenzene from a neutron source for 48 hours. It was then extracted with a 10.53-millimolar aqueous solution of NaBr. The aqueous extract was evaporated to dryness, and the resulting $NaBr^*$ dissolved in 96% alcohol and transferred to a 100-ml measuring flask. Five ml of this solution were titrated with 0.1 N $AgNO_3$. The resultant $AgBr^*$ precipitate was transferred quantitatively to a filter and served as a standard.

One tenth of a mole of inactive C_3H_7Br was dissolved in 96% alcohol in a 50-ml measuring flask. The experiment was begun 36-48 hr after the irridiation of the bromobenzene had been completed. In this time the 18-min and 4-hr isotopes of bromine had almost completely decomposed. The experiments were conducted with nearly pure 34-hr Br^{82}. The 95 ml of $NaBr^*$ solution (10 millimolar), were heated in the reaction vessel to the required temperature, and 5 ml of the alcohol solution of C_3H_7Br were poured in. This made up 100 ml of a solution containing 10 millimoles each of $NaBr^*$ and C_3H_7Br.

A cross-sectional diagram of the experimental apparatus is shown in Figure 1. The reaction vessel 1 with the reflux condenser 4 was placed in flask 2, which served as a vapor bath. This flask, which was provided with a reflux condenser 3 connected by means of a ground glass joint, had been filled earlier with a liquid of appropriate boiling point. In the experiments described below, ethyl ether, chloroform, ethyl alcohol, and water were used for this purpose. The temperature was checked on the thermometer 5. The $NaBr^*$ and C_3H_7Br solutions were introduced into the reaction vessel with the aid of a pipette through the reflux condenser 4. For the latter operation the stopper 6 was taken out for a short time.

At the specific moments when it was necessary to remove the stopper for analysis, air was blown through the tube and cock 7, with the result that part of the reacting solution was forced out through tube 8 into the burette 9. Then, by opening clamp 10 air was injected, and a measured volume of the solution (5 ml) was transferred into the separatory funnel 11. To separate the NaBr from the C_3H_7Br quantitatively, we proceeded in the following manner. The 5 ml of solution in the separatory funnel were cooled and shaken out after the addition of 4 ml of water and 4 ml of benzene. In the funnel two layers formed, the lower being water-alcohol, and the upper benzene. The lower layer was poured out of the funnel, and the remaining benzene layer was washed 2-3 times in water. The results of several analyses of these two layers are cited in Table 1.

As Table 1 shows, the methods used by us permit the quantitative separation of the reacting substances. The loss of propyl bromide as a result of evaporation is explained by the fact that the mixture was not cooled in the first experiments. This loss does not play a substantial role, since in all the experiments we carried out an analytical determination of C_3H_7Br and introduced a correction for evaporation.

The water-alcohol layer was titrated with 0.1 N $AgNO_3$, and the $AgBr^*$ precipitate was transferred quantitatively to a filter and its activity determined by means of a counter.

The benzene layer with 10 ml of a concentrated alcohol solution of alkali was sealed in a tube and heated at 100° for 3 hr. During this time the propyl bromide was completely saponified. When the ampule was opened, the water-alcohol layer was removed and the benzene layer washed three times with water, then added to the water-alcohol layer. To the latter was added a small excess of nitric acid, after which the content of bromine ions was determined by titration with 0.1 N $AgNO_3$. The $AgBr^*$ precipitate was transferred to a filter, and the activity of bromine was determined on a counter. The activity of the standard was determined simultaneously. All the activities were referred to the moment of time corresponding to the beginning of the isotopic exchange reaction.

The results of our experiments at different temperatures are cited in Table 2.

In the case when an isotopic exchange reaction is bimolecular, and the reacting substances are taken in equimolecular quantities, the constant should be calculated from the formula:

$$k = \frac{11.5}{t} \lg \frac{1}{1 - 2x/c} \qquad /1/$$

Here x/c is the ratio of the activity of $AgBr^*$ obtained from the $C_3H_7Br^*$ to the activity of the standard.

Figure 2 shows that the ratio x/c as t increases tends toward 0.5. The experimental results shown in Figure 3 are plotted on the coordinates $-\lg (1-2x/c)$ and t.

The experimental points lie satisfactorily close to straight lines to indicate the applicability of formula /1/ to the given case. From the slope of the lines we calculated the constants for the velocity of the isotopic exchange reaction which are reproduced in the last column of Table 2. The dependence of the velocity constants on temperature is plotted in Figure 4 on the coordinates lg k and 1000/t. The experimental points lie on a straight line. Calculated from the slope of the line, the activation energy E = 18,000 cal/mole.

If in the case being investigated we take $\sigma = 3 \cdot 10^{-8}$ and the steric factor p = 0.01, then the value of activation energy found is in satisfactory agreement with the theory of the activated complex.

The isotopic exchange reaction in the given case is probably linked with the ionization of propyl bromide according to the scheme:

$$C_3H_7Br \rightleftarrows C_3H_7^+ + Br^- \qquad /2/$$

With the formation of molecules, $C_3H_7Br^*$ can be formed. This point of view is confirmed by the experiments of Ewans and Sugden (8), as well as by the recently published work of Gand (9), in which he studied the dissociation into ions of ethyl iodide in aqueous solutions. By the electrical conductivity of these solutions he succeeded in demonstrating that the degree of dissociation of C_2H_5I at room temperature has a value of the order of 10^{-4}.

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Table 1. Check of the Completeness of the Separation of NaBr and C_3H_7Br

	NaBr, in Millimoles			C_3H_7Br, in Millimoles		
Expt No	Intro-duced	Lower Layer	Upper Layer	Intro-duced	Lower Layer	Upper Layer
1	4.97	4.94	0.02	4.50	0.01	4.43
2	0.72	0.714	0.003	0.46	0.002	0.394
3	0.72	0.712	0.003	0.44	0.002	0.395

Table 2. Kinetics of Bromine Exchange Between C_3H_7Br and NaBr*

		Activity				
Temp in °C	t, in Min	C H Br*	NaBr*	Σ Br*	Standard	$k \cdot 10^4$ Liters/Mole·Sec
35	5	2	202	204	204	
	120	17	190	207	204	0.213
	1,110	28	178	206	204	
	1,230	36	170	206	204	
61	25	2	172	174	172	
	85	19	153	172	172	
	265	42	138	180	172	
	470	65	117	182	172	2.13
	650	65	106	171	172	
	840	73	100	173	172	
	1,140	79	94	173	172	
	1,440	82	89	171	172	
79	15	31	406	437	437	
	30	32	332	364	437	
	45	73	361	434	437	
	60	75	357	432	437	8.4
	75	80	328	408	437	
	90	85	310	395	437	
	120	96	286	382	437	
	180	106	272	378	437	
	420	130	223	353	437	
100	15	41	146	187	188	
	30	58	131	189	188	
	50	76	115	191	188	36
	100	89	100	189	188	
	180	90	97	187	188	

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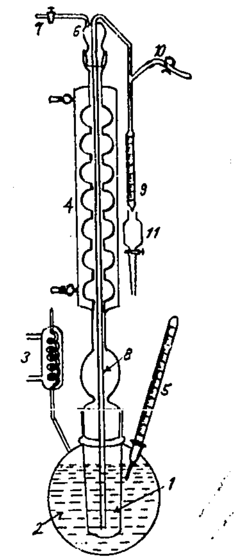

Figure 1. Diagram of Apparatus for Experiments on Isotopic Exchange

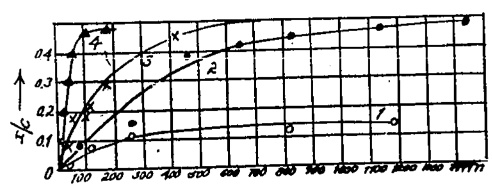

Figure 2. Kinetics of Isotopic Exchange: 1 - at 35°, 2 - 61°, 3 - 79°, 4 - 100°.

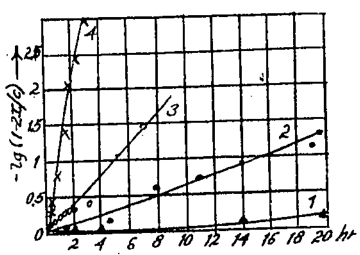

Figure 3. Increase of Activity of Propyl Bromide With Time on the Coordinates -lg(1-2x/c) and t

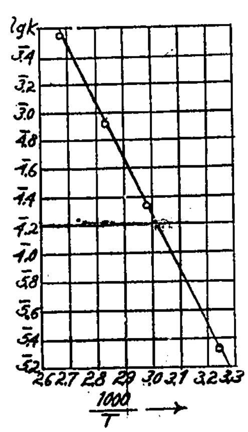

Figure 4. Dependence of Rate of Isotopic Exchange on Temperature, on Coordinates lg k and 1000/T

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